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ORGANIC MOLECULES IN SPACE

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I. INTRODUCTION

The detection of complex organic compounds in meteorites and in ancient rocks plus the synthesis of a variety of organic molecules including amino acids from simple gases has been described in previous chapters. These observations have resulted in the intensive and so far fruitful efforts to fill the gap between the simple gases, water, ammonia and methane, and the simplest living cell. In this, Chapter I indicate the possibility of a somewhat different approach to the question of chemical evolution. Observational evidence for the occurrence of some organic compounds in space is presented and the likely existence of more complex molecules as yet undetected or unidentified is pointed out. This implies that massive solid objects, namely; planets and asteroids were accumulated from material which already contained a variety of organic compounds. The extent to which such molecules were preserved throughout the accumulation process is a major question. However, only a brief

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discussion will be given, as it takes us into new areas of cosmogony of an essentially non-chemical nature.

The objects or regions of the galaxy that will concern us are: (1) comets, (2) interstellar space (3) pre-stellar nebulae and (4) cool stellar atmospheres. The primordial solar nebula in which the planets accumulated is a particular case of a pre-stellar nebulae but is by no means unique. During the lifetime of the galaxy similar objects must have appeared billions of times.

It is appropriate to conclude this introduction with an account of a cosmogonic hypothesis which relates all of the possible sources of molecules.

The brightest, hot stars in the Milky Way cannot have been shining for more than a few hundred thousand years with their available energy supply. This is an insignificant fraction of the age of the Galaxy which is about 10 billion years. Other stellar age indicators require continuous star formation throughout the galaxy, Spitzer (1968a). Star formation takes place by the development of interstellar clouds of gas and solid grains and their subsequent collapse into stars. Several lines of evidence demonstrate the ejection of matter from stars into space either continuously or in bursts as with novae and supernovae. Thus, there is a sequence of stars forming from interstellar matter and then ejecting material back into space. This material later takes part in subsequent star formation.

At the end of the collapse stage of the prestellar cloud a fairly dense nebula with a temperature in the neighborhood of 1000°K must develop. An approximate molecular equilibrium will occur with the composition depending upon density and temperature. When the collapse ceases the temperature will drop to a low value determined by the energy input from the newly formed star. At some point the temperature becomes sufficiently low that a composition becomes "frozen in". Planets and meteorites could accumulate throughout the entire later stages of the nebula but comets must form during the cold stage because of their volatile nature. Because of their small mass and low temperatures comets would be expected to preserve with minimum transformation the composition of the material out of which they and planets formed. Cometary molecules thus represent some mixture from all sources of molecules in the galaxy.

The material which went into the formation of the planets also represents matter from many sources of molecule. The extent to which complex molecules could withstand temperatures and excitation conditions which were experienced from their time of formation to the time they became part of the earth's crust determined the organic composition of the primordial crust before terrestrial chemical evolution started.

II. COOL STELLAR ATMOSPHERES

Stars show an extremely wide range of atmospheric temperatures, Aller (1963). For the coolest stars, some of which are variable in brightness, the lowest temperatures found are about 1500°K . These are stars of spectral class M, which have carbon/oxygen ratios less than unity and whose spectrum is dominated by absorption bands of TiO. For our purpose the important class of stars are the so-called carbon stars. Their spectra show a marked difference in appearance from the stars of type M. The spectrum is dominated by the C_2 Swan bands and an analysis indicates a C/O ratio greater than 1.5. Because of the excess of carbon over oxygen, carbon is not nearly completely combined as CO and a large number of carbon compounds are possible.

A major factor in molecular equilibrium calculations is the temperature of the atmosphere. Effective temperatures of carbon stars, based on the total radiation from a star, are about 2500°K for the coolest stars. Vibrational temperatures are several hundred degrees less and may be 2000°K or somewhat lower.

No detailed models of carbon star atmospheres have been computed but an estimate of their characteristics can be obtained from the M type giant stars with comparable temperatures and luminosities. For these stars the pressure region of interest is $10 - 10^4$ dynes/cm² or 10^{-2}

to 10 Torr. The importance of carbon compounds in the carbon star sequence is emphasized by the identification of C_3 and S_1C_2 in addition to the major role of C_2 in their spectrum.

The usual procedure for computing chemical equilibrium in stellar atmospheres is to write an equation for each element considered in the analysis. For hydrogen this has the form

$$P(H) = p(H) \left[1 + \frac{2p(H)}{K(H_2)} + \frac{p(O)}{K(OH)} + \frac{p(N)}{K(NH)} + \frac{p(C)}{K(CH)} + \frac{p(O)p(H)}{K(H_2O)} \right. \\ \left. + \frac{p(C)p(H)}{K(CH_2)} + \frac{p(H)p(C)p(O)}{K(H_2CO)} + \right]$$

$P(H)$ is the fictitious pressure of the element which would occur if the element existed only as the neutral atom and $p(H)$ is the actual partial pressure at equilibrium. The K 's are the equilibrium constants defined by

$$K_{ABC} = \frac{p(A)p(B)p(C)}{p(ABC)}$$

Similar equations occur for each element. There is a term in the analyses for each molecule in which the element occurs. Equilibrium constants are taken from experiment when possible, or are calculated from the molecular constants. Detailed treatments of this procedure are given by Tsuji (1964) and by Morris and Wyller (1967) for carbon stars. A different approach to determination of

a complex equilibrium has been formulated by White et al (1958) in which the free energy function of the system is minimized by varying the concentration of each species. This method has been employed by Dayhoff et al (1967) for studying prebiological atmospheres.

Table I has been prepared from unpublished calculations by Tsuji for the composition $H:C:N:O = 10^5:18:1:10$ for pressures of 10^2 and 10^4 dynes/cm² and a variety of temperatures. In these calculations only H, C, N and O were considered. No metals, silicon or sulfur were introduced in the atmosphere. These are the cosmically abundant elements which would affect the chemistry. Because relative abundances in carbon stars are not the same as in the sun, for example the alkaline earths and rare earths appear enriched, some of these elements may also be important. However, the trend of these calculations should give a proper indication of carbon compounds to be expected. Morris and Wyller included silicon and used atomic abundances based on later and improved estimates of carbon star composition. However, only a few triatomic molecules were included. Dolan (1965) calculated molecular equilibrium in stars including one carbon star composition. His results were essentially limited to H, C, N and O and included diatomics plus HCN and CH₂. In addition to these calculations, an extrapolation of the calculations of Duff and Bauer (1962) suggests that

benzene may occur to the extent of 1 part in about 10^8 .

All the above assumed thermodynamic equilibrium which is probably a reasonable approximation. A more serious restriction may be the use of constant temperature and pressure instead of a model atmosphere in which both physical parameters increases from the boundary of the atmosphere inward. This refinement has been carried out for M stars by Vardya (1966).

Several analyses of carbon condensation in carbon stars have been carried out following the initial work of Hoyle and Wickramasinghe (1962). Later papers, Donn et al (1968), Kamjo (1966), (1969), and Friedemann and Schmidt (1967) have improved the calculations and taken the nucleation process into account. It was shown in these investigations that graphite grains of a few hundred angstroms could well be expected to form in the cooler stars of the carbon sequence. Friedemann and Schmidt and Wickramasinghe et al (1966) showed that such grains could be ejected from the atmosphere by radiation pressure. The latter paper also pointed out that the grains could carry a small but significant part of the atmosphere with them. The process of mass ejection in M giant stars is well established, Deutsch (1960) Weymann (1963). A similar process in the carbon stars would supply a copious source of carbonaceous material to interstellar space as was pointed out by Tsuji (1964).

Closely related to the phenomena of molecular equilibrium and particle formation in cool stellar atmospheres is the role of similar phenomena in pre-stellar and circumstellar clouds. Infrared observations have detected objects with strong intensity at wavelengths of several microns but with weak or no visible radiation. Brief reviews have been given by Johnson (1967) and Feldmann et al (1966). There appear to be three classes of infrared objects. These are; very cool M giant variables; extremely dense interstellar clouds, and cool circumstellar clouds that may be planetary systems in an early stage of formation. There is much evidence for solid particles and molecules associated with these clouds as well as evidence for the ejection of material from these clouds into interstellar space, Herbig (1969). These objects presumably are associated with solar type stars and primordial nebula with a carbon to oxygen ratio less than unity. However, the discussion of Section 3 shows that complex organic compounds formed early in the history of the solar system, probably prior to or during the accumulation of comets and meteoritic objects. Consequently organic molecules could also form in the infrared objects associated with star and planet formation.

3. Comets and the Primordial Solar Nebula

The comet family (Richter, 1963) consists of astronomically small (~ 40 km diameter, $10^{15} - 10^{19}$ gm) objects which readily evolve large quantities of gas and dust when they approach the sun. About 600 individual comets have been identified when they came within 4 A.U. of the sun. The total number must be enormously larger. There must be a large storehouse of comets at larger distances from which they gradually feed into the inner solar system where they are associated with then gradually disintegrate. Various statistical analysis suggested from 10^7 to 10^{11} .

No complete theory of the origin, structure and composition of comets exists. It is generally believed that they were formed in the early stages of the solar system although an alternative hypotheses of formation interstellar clouds and subsequent capture by the sun has been proposed. If they are indeed associated with the early solar system, comets tell us much about the composition of the primordial solar nebula. Because the solar nebula is believed to have formed from an interstellar cloud the alternative explanation still tells something about the early solar system, although the interpretation is not as direct.

The characteristic observational phenomenon indicating the presence of a comet is the head or coma, an extremely diffuse cloud of gas and dust. A tail, which is the most

prominent feature of bright comets, is generally missing from the fainter, short period comets. Embedded in the coma is the nucleus. This is the permanent part of a comet which revolves around the sun and is the source of coma and tail material. Our only knowledge of the composition of the nucleus comes from spectroscopic observations of coma and tail.

Table 2 shows the molecules identified in comets, listed in the coma in order of appearance as the comet approaches the sun and in the tail the order is generally that of decreasing intensity. The ultraviolet Lyman alpha line of atomic hydrogen has been detected in great strength in two recent bright comets by orbiting spacecraft. The dust continuum arises from scattered sunlight. A very close correspondence of the intensity distribution within molecular emission bands with that of the solar continuum indicates that the molecular emissions result from resonance fluorescence.

The composition and structure of the nucleus must be such as to yield the observed radicals, account for the gas and dust production, and be able to explain the dynamical properties of comets. Whipple's (1950,1963) icy nucleus and its further development, Donn (1963,1967), provides a model that appears to meet these requirements and also to be consistent with an accumulation process in the primordial solar nebula. Because the nucleus is a volatile object the temperature had to be low at all times during and since its

formation, Huebner (1965). Further, because of its small mass, pressures were also generally low, hence no substantial chemical changes in comets have taken place since their origin.

The composition of icy cometary nuclei can be estimated from molecular equilibrium calculations of the primordial nebula. In "The Planets" Urey (1952) considered the equilibrium of the solar nebula under several conditions and cites earlier work. Since then more extensive investigations have been carried out for arrays of about one hundred molecular species. The most useful for the present purpose are those of Tsuji (1964) and of Lord (1965). Table 3 summarizes these results and is a modified form of Urey's calculations.

Two factors may have seriously modified the composition of the solar nebula from the equilibrium values, Fowler et al, (1962), Donn (1968). Radioactive nuclei were much more abundant at the time of formation of the solar system about 5 billion years ago than they are at present. The half life of U^{238} is 7×10^8 years and therefore $N_5 = 1100N_0$. In addition, there is evidence for short lived radioactive elements with half lives $t \sim 10^5$ years that were present in the early solar system.

Of more significance for producing the non-equilibrium effect may have been the energetic corpuscular radiation from the primitive sun. Qualitative considerations indicate that significant chemical effects should have occurred. During this period the energy flux of energetic protons has been estimated

at 10^{45} ergs. If all the energy were absorbed by the nebula, it would correspond to 10^{57} eV. The effects of radiation is measured in terms of the G value for a reaction, the number of molecules destroyed or formed per 100 eV of radiation absorbed. Although G values show a considerable spread and depend upon the medium and its detailed composition, a reasonable value is $G \sim 1$. This leads to a conversion of the thermodynamically stable compounds to the extent of 10^{55} molecules. With a mean molecular weight of 20, this is equivalent to 3.5×10^{32} gm or about two solar masses. If only a fraction of the radiation were absorbed, a substantial proportional of the material in the solar nebula would have been transformed.

Some idea of the ultimate composition of comets may be obtained from experiments on chemical composition of irradiated, condensed gases and the related experiments on the condensation of dissociated gases, Bass and Broida (1960). In the latter case, a small concentration of radicals are obtained in addition to more complex and more reactive molecules. Warm-up of the condensed films yielded an additional array of molecules. It is not clear in most instances whether these existed as such in the condensed matrix or were recombination products produced as the solid warmed and vaporized. Condensation of discharged methane-nitrogen mixtures has yielded the following molecules, Glasel (1961):

acetylene, ethylene, ethane, butadiene, propylene, propane, and butene.

Dissociated water vapor, when condensed in a cold trap, produces a high percentage of hydrogen peroxide, H_2O_2 , plus the HO_2 radical. The formation of the super-peroxide H_2O_4 has been claimed but recent work does not support such a molecule. The production of such unstable species as HO_2 , HCO , $HONO$, NH , NH_2 and almost certainly similar as yet unidentified compounds by photolysis of simple mixtures in the laboratory again suggests the variety of molecules to be expected in the primordial condensed gases.

All these possible contributions to cometary material are combined in Table 4 to yield a suggested composition of the cometary nucleus. The species listed in Table 2 demonstrate the occurrence of significant amounts of carbon compounds in comets. The restriction of observations to the visible spectrum and the absence of laboratory spectra for carbon polymers larger than C_3 , suggest that parent molecules containing more than three carbon atoms may also occur in comets. It must be emphasized that no single model can explain all comets. For Comet Morehouse 1908 III, and Comet Humason 1962 VIII, carbon monoxide appears to have been the dominant constituent. The organic compounds in meteorites described in Part II, Chapter 3, is strong evidence for their occurrence in the primordial nebula. There is therefore good

reason to expect complex organic molecules in comets as well.

4. Interstellar Space

The sun is about two-thirds of the distance from the center of our galaxy to the outer edge and lies almost in its central plane. Although the overall star distribution is spherical, the most luminous and hottest stars, and the diffuse matter between the stars are highly concentrated to the galactic plane. Interstellar chemistry is concerned with this median region or galactic disc as it is generally known.

Several modes of analyses, Spitzer, (1968b) yield total densities of interstellar matter as about $5 \times 10^{-24} \text{ g/cm}^3$. Wide angle photographs of the Milky Way show the very irregular distribution of obscuring clouds and of luminous region in the galaxy. In addition, high resolution spectra show that the absorption lines of interstellar molecules may contain several Doppler displaced components. This is evidence for a discrete velocity distribution of the gas and very likely a discrete spatial distribution also. It is convenient, although oversimplified, to describe the distribution of interstellar matter by a random cloud model. According to this picture a kiloparsec ($3 \times 10^{21} \text{ cm}$) line of sight intercepts five to ten clouds with mean diameters of 10 parsecs each. Within the cloud there are ten hydrogen atoms per cm^3 and between clouds about 0.1 atom per cm^3 . The radio

line of the hydroxyl radical, OH, has recently been detected in obscuring or dust clouds with radii as small as 0.5 pc and densities probably near 1000 H atoms/cm³.

Most of the information of the composition of the gas is based on spectra obtained in the visible region. With the development of radio astronomy and more recently, vacuum ultraviolet spectroscopy from rockets, additional atoms and molecules have been observed. The list of all elements and compounds observed in interstellar space is presented in Tables 5, 6, and 7. Tables 5 and 6 list the species observed in the visible, in absorption and in emission respectively. Table 7 shows the constituents detected more recently by radio or ultraviolet observations. Abundances in interstellar space conform generally to a so-called cosmic abundance distribution, Suess and Urey (1956), Cameron (1959) derived from a variety of celestial sources, including the earth. It is reasonable to apply this result to obtain an approximate complete composition for the interstellar medium. The more abundant elements and their approximate average interstellar number density appear in Table 8.

The significant presence of carbon compounds appears in interstellar space also. Not only are two of the three observed diatomic radicals the compounds CH and CN, but the most complex molecule so far found in interstellar space is the organic compound, formaldehyde.

In addition to the sharp lines, optical spectra reveal some 25 broader absorption features. None have yet been identified but several possibilities have been considered a few of which, Duley (1969 a,b), Herzberg (1969), Johnson (1965), are related to the subject of this chapter.

The third constituent of the interstellar medium is the material producing the obscuration and reddening of starlight. Again, many suggestions have been made as to the nature of this material, generally referred to as interstellar grains. The proposals include (a) mixtures of condensed gases, mainly water, ammonia and methane, (b) silicates, (c) graphite (d) metals (e) condensed gas mixture on graphite core. Detailed discussions of such particles are given by Greenberg (1968) and Wickramasinghe (1967).

The prevailing theory considers classical scattering and extinction by small particles and requires particles with dimensions from about 300 \AA to 3000 \AA depending upon composition. A recent proposal by Platt (1956) based upon a quantum mechanical interaction indicated that disordered molecular aggregates of about 20 \AA diameter could produce the extinction. This suggestion has been further developed by Donn and his associates (1968, 1969, 1970). It was shown that arrays of polycyclic hydrocarbons containing about 5 or more rings have continuous extinction through the visible region of the spectrum very similar to the interstellar extinction as shown in Figure 1 by Donn and Krishna Swamy (1969).

Infrared and ultraviolet absorption coefficients for such molecules are consistent with the extinction ratio for these spectral regions observed in interstellar space. From the discussion in Section 2 on molecules in carbon stars, such stars may be the source of these compounds. The analyses of graphite formation reviewed there also makes the occurrence of polycyclic aromatics likely.

Clar (1964) has called attention to the sequence of isomers with maximum chemical and thermal stability, Figure 2: benzene, diphenyl, triphenylene, dibenzopyrene, tribenzoperylene, tetrabenzoanthanthrene and hexabenzocoronene. The largest member has been described by Clar in the following way. "Hexabenzocoronene which does not melt even above 700°C , is insoluble in all conventional solvents and can be formulated with sextets only, can therefore be considered as a particle of graphite." In a crystal nucleation and growth process for the formation of graphite grains in stellar atmospheres as described in Section 2, the carbon skeleton of these or similar polycyclics or heterocyclic aromatics could well be among the growing clusters. Conditions for the formation of such molecules are less stringent than for the growth of graphite grains of a few hundred angstroms. Whatever process would eject graphite into space also works for these species. It appears possible to explain all features of the wavelength dependence of interstellar extinction, as well as interstellar polarization by these molecules. They have the

advantage of being stable up to about 600°K for the smaller molecules and to 1000°K for the largest. Further experiment on the optical, thermal and photochemical properties of these types of molecules are under way at Goddard. Thus, in addition to small organic molecules and radicals now known to be present in interstellar space, there is a possibility of very much larger molecules also. An array of aromatics containing at least about five rings but with a much larger upper limit to the number of rings could be present. These would not be pure hydrocarbons but should include other atoms both in the ring structure and in the side chains replacing hydrogen.

Irradiation of the van de Hulst ice model of the interstellar grain is another, somewhat more hypothetical, source of organic material in interstellar space. The suggested composition given by van de Hulst (1948), Greenberg, (1968) was 100 parts H_2O , 30 part H_2 , 20 parts CH_4 , 10 parts NH_3 , 5 parts M_gH and other metallic compounds. With a radii under 0.5μ , the particle dimensions are the order of the skin depth and the ultra flux will penetrate the entire grain. In addition, the low energy cosmic rays would contribute to chemical changes in the grain. Measurements from spacecraft indicate a cosmic ray flux near one Mev that may be four orders of magnitude greater than previously considered. Both types of radiation, acting over grain lifetimes of 10^7 to 10^8 years would produce radicals like OH, NH, CH_3 , etc. These

would recombine in a random fashion within the grain to gradually polymerize the particle and build up more complex organic molecules. Experiments by Oro (1963) on the irradiation of a water, ammonia, methane film by 5 Mev electron yielded about 20% non-volatile organic matter including simple amino acids. Further experiments to determine the type of change and the rate are being started at Goddard. Such chemical changes would also effect the thermal stability and optical properties of the grain and have significant astrophysical consequences.

4. Summary

Spectroscopic studies of comets and interstellar matter demonstrate the presence of simple organic molecules in interplanetary and interstellar space. Difficulties in detecting or identifying larger carbon compounds in either case suggest that presently known molecules are not the most complex that occur.

Several proposals attempting to explain the extinction of starlight in interstellar space suggest some type of carbonaceous material may be present. The form of the carbon runs from pure graphite flakes through polymerized water, ammonia, methane, etc. grains to polycyclic aromatic molecules.

Laboratory analyses of meteorites described in Part II, Chapter 3, indicate the large variety of quite complex organic material that is found. Although the origin is unknown, their presence in meteorites is indicative of formation in the solar nebula or earlier stage of galactic evolution. On the basis of their laboratory experiments Studier et al (1968) have proposed hydrocarbon formation via a Fisher-Tropsch mechanism on particulate matter which condensed in the primordial nebula.

As indicated in the Introduction, the presence of organic matter from a variety of cosmic sources may all be closely related. Our knowledge of galactic evolution

and space chemistry is too incomplete at present to draw definite conclusions. But whether organic matter throughout the galaxy has a common origin or formed independently in several places, we know it does occur. The question of how much and in what form these compound survived during the process of earth accumulation and crystal formation is the most significant issue remaining. However, the thermal stability of the more complex molecules and the likelihood of some polymerization suggests that a primordial organic residue remained on the surface of the earth after the crust and atmosphere formed. Some consideration of this problem appears in the paper by Oro (1965) and the discussion following his paper. This raises the final questions of this discussion of organic molecules in space: What was the probable nature of the residual organic material and to what extent could a scheme of terrestrial biochemical evolution proceed from such initial circumstances?

REFERENCES

- Aller, L. H., 1963, *Astrophysics, The Atmospheres of the Sun and the Stars*, 2nd Ed. (Ronald Press, N.Y.), Chapter 3.
- Bass, A. and H. Broida, 1960, *Production and Trapping of Free Radicals* (Academic Press, New York).
- Cameron, A.G.W., 1959, *Astrophys. J.* 129, 676, A Revised Table of Abundances of the Elements.
- Clar, E., 1964, *Polycyclic Hydrocarbons*, 2v (Academic Press, N. Y., London, V. 1, Chapter 6.
- Dayoff, M. O., E. R. Lippencott, R. V. Eck, and G. Nagarajan 1967, *Thermodynamic Equilibrium in Prebiological Atmospheres of C,H,O,N,P,S and Cl*, NASA SP-3040 (National Aeronautics and Space Administration, Washington, D. C.)
- Deutsch, A. J., The Loss of Mass from Red Giant Stars, In: Greenstein, J. L. ed. *Stellar Atmospheres* (Univ. of Chicago Press, Chicago) 1960, pp. 543-568.
- Dolan, J. F., 1965, *Astrophys. J.*, 142, 1621, Stellar Molecular Abundances.
- Donn, B., 1963, *Icarus*, 2, 396, The Origin and Structure of Icy Comet Nuclei.
- Donn, B., 1968a *Astrophys. J.*, 152, L 129, Polycyclic Hydrocarbons, Platt Particles and Interstellar Extinction.
- Donn, B., 1968b *Cosmic Chemistry*, In: G. Mead and W. N. Hess, ed. *Introduction to Space Science* (Gordon and Breach, N. Y.), pp. 501-528.
- Donn, B., and K. S. Krishna Swamy, 1969, *Physica*, 41, 144, Extinction by Interstellar Grains, Mie Particles and Polycyclic Aromatic Hydrocarbons.
- Donn, B., L. J. Stief and W. A. Payne, 1970, *Spectroscopy, Pyrolysis and Photolysis of Polycyclic Aromatic Molecules* (to be published).
- Donn, B., N. C. Wickramasinghe, J. P. Hudson and T. P. Stecher 1968, *Astrophys. J.* 153, 451, On the Formation of Graphite Grains in Cool Stars.
- Dufay, J., 1957, *Galactic Nebulae and Interstellar Matter*, Trans. A. J. Pomerans (Philosophical Library, N.Y.).
- Duff, R. E. and S. H. Bauer, 1962, *J. Chem. Phys.* 36, 1754 Equilibrium Composition of the C/H System at Elevated Temperatures.

Duley, W. W., 1969a, *Physica* 41, 134, Spectra of Impurities in Interstellar Grains.

Duley, W. W., 1969b, *Nature*, 224, 785, Possible Identification of the Diffuse Interstellar Absorption Band at 4430 Å.

Feldman, P.A., M. T. Rees and M. W. Werner, *Nature*, 224, 752, Infrared and Microwave Astronomy.

Fowler, W., J. L. Greenstein and F. Hoyle, 1962, *Geophys. J.* 148, Nucleosyntheses during the Early History of the Solar System.

Friedemann, Chr. and K. H. Schmidt, 1967, *Astron. Nachs.* 289, 223, Zur Entwicklung von Graphitteilchen in den Atmosphären von Kohlenstoffsternen.

Glaser, T., 1961, *Proc. Nat. Acad. Sci.*, 47, 174, Stabilization of NH in Hydrocarbon Matrices and its Relation to Cometary Phenomena.

Greenberg, J. M. 1968, Interstellar Grains, In: Middlehurst, B.M. and L. H. Aller, *Nebulae and Interstellar Matter* (University of Chicago, Chicago, Ill.), 221-364.

Herzberg, G. 1969, Symposium on Laboratory Astrophysics, Lunteren (unpublished)

Hoyle, F. and N. C. Wickramasinghe, 1962, *Monthly Notices, Roy. Astron. Soc.*, 124, 417, On Graphite Particles as Interstellar Grains.

Herbig, G. H., 1969, In *Liege Symposium, Pre-main-Sequence Stellar Evolution*, Liege, 1969, to be published.

Huebner, W. F., 1965, *Zt. Astroph.* 63, 22, Über die Gasproduktion der Kometen.

Johnson, F., 1965, Diffuse Interstellar Lines and the Chemical Characterization of Interstellar Dust, In: Greenberg, J.M., and T. P. Roark eds. *Interstellar Grains*, NASA SP-140 (NASA, Washington, D. C.), pp. 229-240.

Johnson, H. L., 1967, *Science*, 157, 635, Infrared Stars.

Kamijo, F., 1966, Supersaturation of Carbon Vapour in the Carbon Stars, In: Hack, M. ed., *Colloquium on Late Type Stars*, Obs. Astronomica di Trieste, Trieste, pp. 252-250.

Kamijo, F., 1969, *Physica*, 41, 163, Supersaturation of Carbon Vapour in the Carbon Stars II.

Kimura, H., 1962, *Proc. Astron. Soc. Jap.* 14, 374, The Effect of Suprathermal Particles on Interstellar Dust.

Lord, H. C., 1965, *Icarus*, 4, 279 Molecular Equilibria and Condensation in a Solar Nebula and Cool Stellar Atmospheres.

Morris, S. and A. A. Wyller, 1967, *Astrophys. J.*, 150, 877, Molecular Dissociative Equilibria in Carbon Stars.

Oro, J., 1963, *Nature*, 197, 971, Synthesis of Organic Compounds by High Energy Electrons.

Oro, J., 1965, Stages and Mechanism of Prebiological Organic Synthesis, In: Fox, S. W., ed., *The Origins of Prebiological Systems* (Academic Press, New York, pp. 137-171).

Platt, J. R., 1956, *Astrophysics J.* 123, 486, On the Optical Properties of Interstellar Dust.

Richter, N. B., 1963, *The Comets*, Trans. by Beer, A. (Dover Publications, N. Y., Methuen & Co., Ltd., London).

Spitzer, L., 1968a, Dynamics of Interstellar Matter and the Formation of Stars. In: Middlehurst, B. M., and L. H. Aller, *Nebulae and Interstellar Matter* (Univ. of Chicago Press, Chicago), pp. 1-64.

Spitzer, L., 1968b, *Diffuse Matter in Space* (Interscience), N. Y.

Studier, M. H., R. Hayatsu and E. Anders 1968, *Geochim. et Cosmochim. Acta*, 32, 151, Origin of Organic Matter in the Early Solar System. I. Hydrocarbons.

Suess, H. E. and H. C. Urey, 1956, *Rev. Mod. Phys.* 28, 53 Abundances of the Elements.

Tsuji, T., 1964, *Ann. Tokyo Astron. Obs.* 2nd Ser. 9, No. 1, Molecular Abundances in Stellar Atmospheres.

Urey, H. C., 1952, *The Planets*, (Yale University Press, New Haven, Conn.) Chap. 4.

van de Hulst, H. C., 1949, *Rech. Astron. Observ. Utrecht*, 11, Pt. 2, The Solid Particles in Interstellar Space.

Vardya, M.S., 1966, *Monthly Notices Royal Astron. Soc.* 134, 347, March with Depth of Molecular Abundances in the Outer Layers of K and M Stars.

Weymann, R., 1963, Mass Loss from Stars, In: *Ann. Rev. Ast. Astrophys.* (Annual Reviews, Inc., Palo Alto, Calif.) p. 97.

Whipple, F. L., 1950, *Astroph. J.* 111, 375, A Comet Model.

Whipple, F. L., 1963, On the Structure of the Cometary Nucleus
In: Middlehurst, B. and G.P. Kuiper, eds. The Moon, Meteorites
and Comets, (Univ. of Chicago Press, Chicago, Ill.) pp. 639-664.

Wickramasinghe, N.C., B. Donn and T. P. Stecher, 1966, Astrophys.
J., 146, 590, A Mechanism for Mass Ejection in Red Giants.

Wickramasinghe, N.C., 1967, Interstellar Grains (Chapman and
Hall, London)

White, W.B., S. M. Johnson, and G. B. Dantzig, 1958, J. Chem.
Phys. 28, 751, Chemical Equilibrium in Complex Mixtures.

TABLE 1

Abundance of Carbon Compounds in Carbon Stars
 $\text{H:C:N:O} = 10^4:18:1:10$
 (Log of partial pressures d/cm^2)

Compounds	$P = 10^4 d/\text{cm}^2$ $T(^{\circ}\text{K})$					$P = 10^2 d/\text{cm}^2$ $T(^{\circ}\text{K})$				
	2510	2290	1940	1440	1008	2520	2290	1940	1440	1008
H_2O	.51 -6	.51 -6	.58 -6	.91 -6	.66 -3	.18 -10	.49 -10	.62 -10	.86 -10	.73 -9
CO	.00 1	1.00 1	1.00 1	1.00 1	.00 1	.00 -1	.00 -1	.00 -1	.00 -1	.00 -1
H_2CO	.42 -8	.49 -8	.55 -8	.66 -8	.87 -8	.74 -13	.23 -12	.52 -12	.66 -12	.87 -12
C	.81 -2	.66 -3	.19 -5	.43 -11	.50 -23	.46 -2	.43 -3	.12 -5	.48 -11	.56 -21
CH	.69 -3	.83 -4	.90 -6	.33 -10	.47 -20	.00 -4	.47 -5	.82 -7	.38 -11	.39 -19
CH_2	.46 -2	.06 -2	.00 -3	.38 -6	.79 -13	.42 -5	.56 -5	.91 -6	.43 -8	.71 -13
CH_4	.82 -4	.45 -3	.37 -2	.15 -0	.90 0	.11 -9	.70 -8	.25 -6	.20 -4	.83 -2
C_2	.55 -3	.50 -4	.04 -6	.12 -12	.80 -27	.85 -4	.03 -4	.91 -7	.21 -12	.65 -23
C_2H	.29 0	.98 -1	.96 -2	.26 -4	.33 -13	.25 -2	.38 -2	.82 -3	.35 -5	.18 -10
C_2H_4	.69 -5	.17 -4	.92 -4	.23 -2	.40 -0	.94 -12	.70 -10	.39 -8	.16 -6	.98 -5
C_3	.84 -3	.22 -3	.45 -5	.85 -10	.57 -24	.79 -4	.51 -4	.26 -5	.99 -10	.34 -18
C_3H_3	.48 -5	.91 -5	.14 -4	.03 -4	.23 -11	.40 -10	.81 -9	.91 -8	.16 -7	.01 -8
C_4H	.25 -2	.27 -2	.59 -3	.26 -5	.57 -18	.50 -5	.20 -4	.32 -4	.45 -6	.28 -11
CN	.04 -1	.54 -2	.45 -3	.88 -6	.36 -12	.75 -3	.41 -3	.42 -4	.91 -7	.25 -11
HCN	.82 -1	.89 -1	.89 -1	.79 -1	.40 -3	.18 -3	.63 -3	.85 -3	.82 -3	.27 -3

TABLE 2
Atoms and Molecules Identified in Comets

Coma	Tail
Dust continuum	Dust continuum
* H, CN	CO ⁺
C ₃ , NH ₂	N ₂ ⁺
C ₂	CO ₂ ⁺
OH, NH, CH	CH ⁺
Na	OH ⁺
Fe, Ni, Ca, K	

* Observed once at < IAU by Orbiting Astronomical Observatory (OAO)

TABLE 3

Compounds in the Primordial Solar Nebula

 $P = 10^{-3}$ ATM
Temperature

Element

298°K

1200°K

H	H ₂ , CH ₄ , NH ₃ , H ₂ O	H ₂ , H ₂ O, H ₂ S
He	He	He
C	CH ₄	CO
N	NH ₃ , NH ₄ ⁺	N ₂
O	H ₂ O	H ₂ O
Ne	Ne	Ne
Si	SiO ₂	SiO ₂ , SiC
S	FeS	H ₂ S
Fe	FeS, Fe ₃ O ₄ Fe ₂ SiO ₄	Fe, Fe ³ C

TABLE 4

A suggested composition of the cometary nucleus

Type of Material	Examples
Volatile, Inorganic	N ₂ , Ne, Ar, H ₂ O, NH ₃ , CO, H ₂ O ₂ , N ₂ H ₄ , H ₂ S
Volatile, Organic	CH ₄ , C ₂ H ₂ , C ₂ H ₄ , HCN, CH ₃ OH, (C ₆ H ₆)
Non-volatile, Organic	Higher aromatics, complex organic molecules, polymerized material
Non-volatile, Inorganic	Silicates, metallic oxides (metals, carbon grains)
Radicals	OH, NH, C ₂ , C ₃ , CH ₂ , HO ₂

TABLE 5

Interstellar Atoms and Molecules, Visible Spectrum in Absorption

Atoms		Molecules	
Na I	3302-3 Å	CH	4300 Å
	5690-6		3890-86-77
K I	7665-99		3146-43-38
Ca I	4227	CN	3874-5-6
Ca II	3933-68	CH ⁺	4233, 4
Ti II	3073		3957
	3229-42		3745
	3283		
Fe I	3720		
	3859		

TABLE 6

Interstellar Atoms: Visible Spectrum in Emission
(H II Regions, Emission Nebula and Planetary Nebulae)

Hydrogen	Silicon
Helium	Sulfur
Carbon	Chlorine
Nitrogen	Argon
Oxygen	Pottasium
Fluorine	Calcium
Neon	Iron
Sodium	

TABLE 7

Interstellar Atoms and Molecules:
Ultraviolet and Radio Spectrum

<u>U. V.</u>		<u>Radio</u>	
Species	Wavelength	Species	Wavelength
O I	1302 A	H	21 cm
C II	1335	OH	18cm, 5 cm
Si II	1526	NH ₃	1.25 cm
Al II	1671	H ₂ O	1.35 cm
		H ₂ CO	6.2 cm, 2.07 cm
		CO	2.6 mm

TABLE 8

Cosmically Abundant Elements

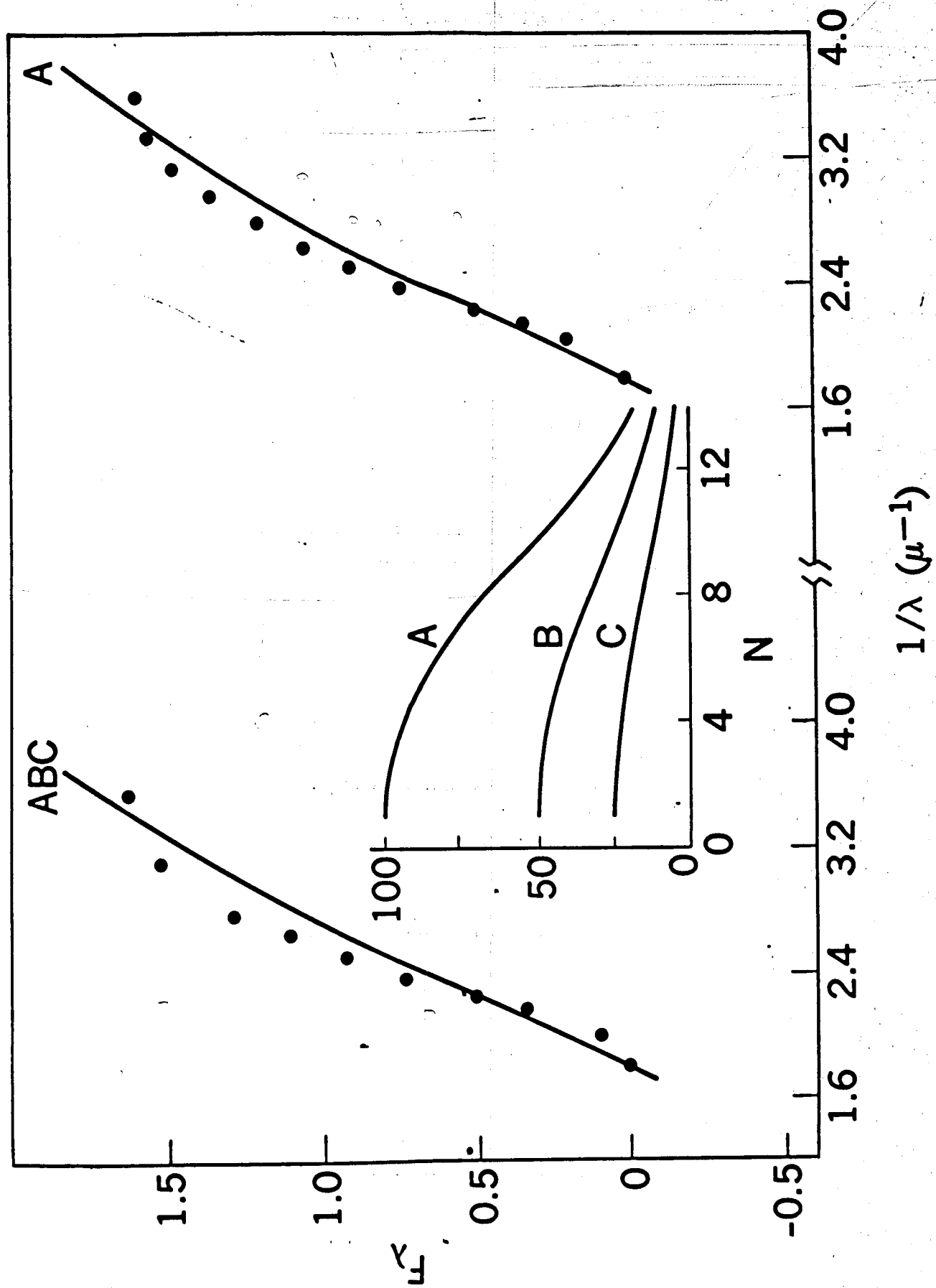
(Suess and Urey, 1956)

Z	Element	Interstellar Density (Atoms/cm ³)	Rel Abundance Si = 10 ⁶
1	Hydrogen	1	4x10 ¹⁰
2	Helium	0.1	4x10 ⁹
8	Oxygen	5x10 ⁻⁴	2x10 ⁷
10	Neon	2x10 ⁻⁴	9x10 ⁶
7	Nitrogen	2x10 ⁻⁴	7x10 ⁶
6	Carbon	10 ⁻⁴	4x10 ⁶
14	Silicon	3x10 ⁻⁵	1x10 ⁶
12	Magnesium	3x10 ⁻⁵	9x10 ⁵
26	Iron	2x10 ⁻⁵	6x10 ⁵
16	sulfur	1x10 ⁻⁵	4x10 ⁵
18	Argon	5x10 ⁻⁶	2x10 ⁵
13	Aluminum	3x10 ⁻⁶	9x10 ⁴
20	Calcium	1x10 ⁻⁶	5x10 ⁴
11	Sodium	1x10 ⁻⁶	4x10 ⁴
28	Nickel	5x10 ⁻⁷	3x10 ⁴
15	Phosphorus	2x10 ⁻⁷	1x10 ⁴
17	Chlorine	2x10 ⁻⁷	9x10 ³
18	Potassium	1x10 ⁻⁸	3x10 ³

FIGURE CAPTIONS

Figure 1. Comparison of interstellar extinction curve and extinction by array of polycyclic hydrocarbons (Donn and Swamy, 1969). The ordinate is the extinction in magnitudes compared to that at 5600 Å. The insert shows the size distribution of molecules comprising the array. The curves A, B and C are for successively less stable groups. The abscissa N is the number of rings in the molecule and the ordinate is the relative number of molecules.

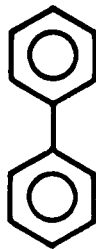
Figure 2. Sequence of most stable polycyclic isomers (graphite precursors).



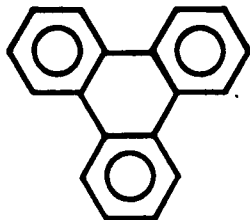
GRAPHITE PRECURSORS



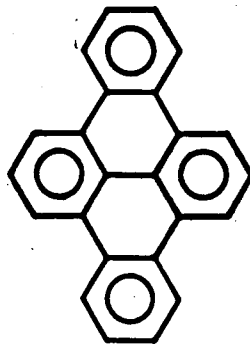
BENZENE



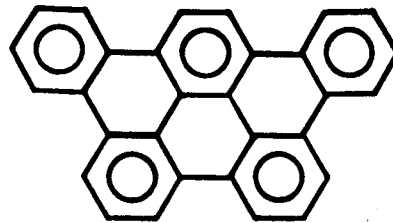
DIPHENYL



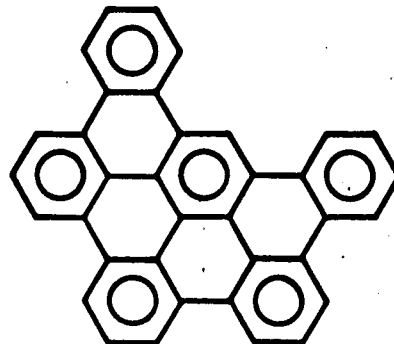
TRIPHENYLENE



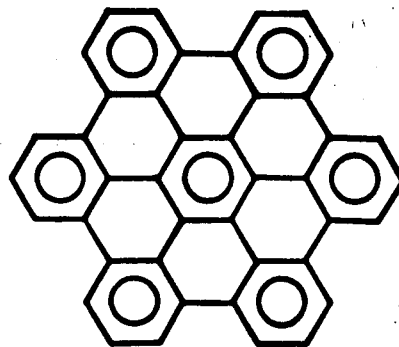
DIBENZOPYRENE



TRIBENZOPERYLENE



TETRABENZANTHANTHRENE



HEXABENZOCORONENE